

5.3100

5(3)

67914

AUTHORS:

Batuyev, M. I., Akhrem, A. A., Matveyeva, A. D.

SCV/20-129-5-21/64

TITLE:

Optical Investigation of the Conformations of Acetyl Cyclohexene and Its Oxide

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5, pp 1038 - 1041 (USSR)

ABSTRACT:

Table 1 shows the physical properties of acetyl cyclohexene and its oxide which was produced by the aid of alkaline hydrogen peroxide (Ref 1, see Scheme). The Raman spectra of both these substances were taken by means of the Soviet 3 prism spectrograph ISP-51 with a central chamber and the Hilger spectrograph Ye612 in the liquid phase. The exciting frequency 4358 Å stemmed from a mercury lamp. The measured frequencies are specified. The presence of frequencies in the region of the triple bond (2096, 2111 cm^{-1}) in the spectra of both substances points to the fact that they still contained residues of the ethynyl compound utilized for their synthesis. i - C frequencies showed that the oxidation of acetyl cyclohexene was incomplete and that the oxidation product is a mixture from acetyl cyclohexene and its oxide. The oxide, how-

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ever, is clearly predominant. It was electronographically confirmed (Refs 2,3) that the carbon atoms of the double bond C_1 and C_2 are placed on or approximately on the same plane. The molecule exhibits half-chair-shaped (polukreslovidnyy) conformations (Ref 4) (see Scheme). The valencies are quasi-equatorial (e') and quasi-axial (a') at the atoms C_3 and C_6 , whereas they are equatorial (e) and axial (a) at C_4 and C_5 . Since the half-chair-shaped confirmation of cyclohexene is energetically by 2.7 kcal/mol more advantageous, and since the rules established by Barton and Khassel' (Ref 7) are evidently still valid for substituted cyclohexenes, the half-chair-shaped confirmation in acetyl cyclohexene is apparently predominant. In this connection, the acetyl group is placed on the plane of atoms $C_1C_2C_3C_6$ or on an approximated plane (see Scheme). There are no reasons for denying the conservation of the acetyl group position in the case of conversion $(I) \rightleftharpoons (II)$. The carbonyl group frequency is divided into 1663 and 1672 cm^{-1} . The ethylene bond frequency is practically not divided into a doublet. The authors are inclined to assume that

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the division of the carbonyl frequency is to be explained by the possible double position of carbonyl with respect to the ethylene formation C=C of the ring, namely, the cis-oid position ((I) \rightleftharpoons (II)) and the trans-oid position ((III) \rightleftharpoons (IV)) (see Scheme). The oscillation frequency of the ethylene bond remains practically unchanged. The oxidation of the acetyl cyclohexene on the double bond leads to the formation of a 3-membered oxide ring



C—C, whose C—C-bond belongs to the 6-membered carbon ring. The half-chair-shaped conformation of the 6-membered ring is conserved in the acetyl cyclohexene oxide (Ref 9). If the above-mentioned position of the acetyl group is conserved, the oxygen atom of the 3-membered ring (see above) is placed on a plane which is perpendicular to the plane $C_1C_2C_3C_6$. The above concepts were concretized by optical data supplied by the authors. It was finally confirmed that acetyl cyclohexene oxide exists in cis-oid (V) \rightleftharpoons (VI) and trans-oid (VII) \rightleftharpoons (VIII) conformations. The causes leading to the formation of both these forms are

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different in acetyl cyclohexene and in its oxide. There are 1
table and 9 references, 3 of which are Soviet.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR (Institute
of Mineral Fuels of the Academy of Sciences, USSR)

PRESENTED: July 15, 1959, by B. A. Arbuzov, Academician

SUBMITTED: July 3, 1959

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BATNITSEV, M. I.; AKHREM, A. A.; MATVEYEVA, A. D.

Optical study of some acetylenic alcohols and their acetates.
Izv. AN SSSR. Otd. khim. nauk no. 12:2201-2207 D '60. (MIRA 13:12)

1. Institut goryuchikh iskopayemykh AN SSSR i Institut organicheskoy khimii im. N. Z. Zelinskogo AN SSSR.
(Acetylene compounds--Optical properties)

5.3400, 5.3100

77914

SOV/79-30-2-65/78

AUTHORS: Batuyev, M. I., Onishchenko, A. S., Matveyeva, A. D., Aronova, N. I.

TITLE: Optical Investigation of the Effect of Hydrogen Bonding on Conjugation in Acrylic and Methacrylic Acids

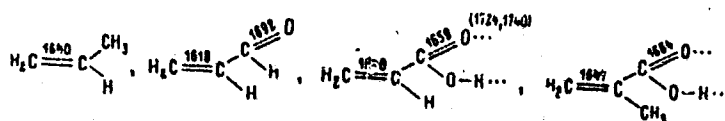
PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 657-661 (USSR)

ABSTRACT: The conjugation of the carbonyl and ethylene bonds more or less weakens (depending on the molecule structure) the ethylene bond, i.e., it decreases its electron density. This manifests itself by the decrease of the bond vibrational frequency, and consequently by the decrease of the bond energy and the increase of the interatomic distance. The study of bond frequency in methylethylene and acrolein showed that the frequency of $C=C$ bond decreased from 1640 cm^{-1} to 1618 cm^{-1} ; and that of $C=O$ bond remained at a high value, (1692 cm^{-1}). In acrylic and methacrylic acids in liquid phase, however, the ethylene bond frequency remains the same, whereas the frequency of the carbonyl bond decreases considerably (to 1659 cm^{-1} and 1664 cm^{-1} , respectively).

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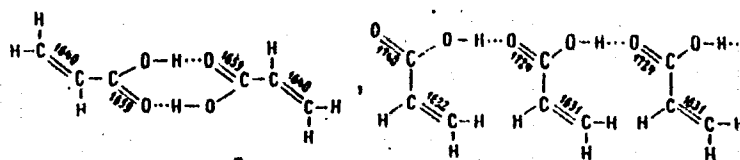
This relationship of the bond frequencies is evidence of a decrease of the effect of the carbonyl bond conjugated with the ethylene bond, which is due to the carbonyl hydrogen bonding. Acrylic acid in liquid phase forms cyclic dimer complexes, and also multiple chain complexes which affect, to a varying extent, the electron density of the conjugated ethylene groups: (1) carbonyl participating in the hydrogen bonding of the dimer ring (1659 cm^{-1}); this carbonyl is most affected by the hydrogen bond, has the least electron density, and therefore shows an insignificant weakening effect only on the ethylene bond; the frequency of the latter remains at 1640 cm^{-1} ; (2) carbonyl in the chain complex, with a greater electron density (1724 cm^{-1}), which affects the conjugated ethylene bond to a greater extent and lowers its frequency to 1631 cm^{-1} ; (3) end carbonyls

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SCV79-30-2-65/78

of the chain complex with the highest electron density (1740 cm^{-1}) which weakens the conjugated ethylene bond to the highest extent and reduces its frequency to 1622 cm^{-1} .



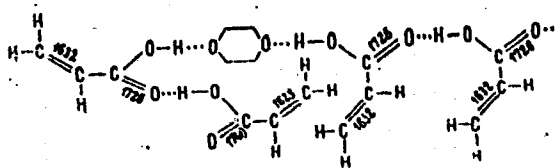
The analysis of spectral data of liquid methacrylic acid showed that the cyclic dimers are preponderant, and the cyclic chain complexes are almost nonexistent in this acid, due, evidently, to steric hindrance by the methyl group. The dissolution of acrylic and methacrylic acid in dioxane caused an opening of the ring; simultaneously, the dioxane and acid molecules formed an associated complex whose carbonyls formed, in turn, hydrogen bonds with other acid molecules, and the $\text{C}=\text{O}$ bond frequencies remained practically unchanged.

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Unassociated carbonyls (as in methyl acrylate and methyl methacrylate) show an electron density nearer to that of the terminal carbonyls or carbonyls inside the chain, than to that of the carbonyls in the cyclic dimer. Hence, the nonparticipation of the carbonyls in hydrogen bonding increases its weakening effect on the conjugated ethylene bond. One of the factors which characterizes this effect is a substantial asymmetry of the electron shell of the carbon atom in the $C=O$ radical which leads to a marked decrease of the shielding effect of the positive nucleus from the side opposite to the oxygen atom ($> \overset{+}{C}=O$) and to a weakening of the ethylene bond. The presence of pairs of nonbonding electrons in the outer shell of the oxygen atom, makes it more susceptible to change under the influence of various factors such as hydrogen bonding, the introduction of substituents, etc., which lead to substantial changes in

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the nature of the carbonyl bond and to corresponding changes in its effect upon the conjugated ethylene bond. ISP-51 spectrograph was used in the determination of the bond frequencies. There are 2 tables; and 4 Soviet references.

ASSOCIATION:

Institute of Mineral Fuels, Academy of Sciences USSR, and Institute of Organic Chemistry, Academy of Sciences, USSR (Institut goryuchikh iskopayemykh Akademii nauk SSSR i Institut organicheskoy khimii Akademii nauk SSSR)

SUBMITTED:

January 22, 1959

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S/020/60/132/03/25/066
B011/B008

AUTHORS: Batuyev, M. I., Onishchenko, A. S., Matveyeva, A. D.,
Aronova, N. I.

TITLE: Optical Investigation of Geometric and Rotatory Isomerism
of Some Dienes

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 3,
pp. 581-584

TEXT: The authors state on the basis of Refs. 1-4 that the flat trans-
form (II) is absolutely prevalent up to 95% in 1,3-butadiene at room
temperature. The cis-form (I) possesses no center of symmetry. At room
temperature it is only admixed to the trans-form. These statements are
confirmed chemically: 1,3-butadiene enters into the Diels-Alder
synthesis only slowly at room temperature. This reaction takes place
much more easily at a temperature rise which corresponds to the
transition of the trans-form into the cis-form. Rotatory isomerism is
also possible in the mono- and di-substituted 1,3-butadienes investi- ✓ B

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Optical Investigation of Geometric and
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B011/B008

gated by the authors. In some cases, however, it is superimposed to the geometric isomerism, as for example in 1-chloro-1,3-butadiene and piperylene (1,3-pentadiene). On the basis of such a superimposition the authors presume the existence of the following 4 isomers: (III), (IV), (V) and (VI) (see Scheme). The trans-forms (III) and (V) predominate here too at room temperature in the liquid phase. They possess no center of symmetry. The symmetric as well as the asymmetric frequencies of their double bonds must therefore appear in their Raman- and IR-absorption spectra. The frequencies must be higher in (V) than in (III). All this was actually established by the authors. They state that the oscillation frequencies of the double bonds of the trans-configurations are higher than those of the cis-configurations. The chemical data are in agreement with these statements. Thus, the cis-configurations of the trans-form (III) do not enter into the Diels-Alder synthesis at $X = Cl, CH_3$ even at a temperature rise, since in this case (III) can only proceed into the cis-configuration of the cis-form (IV), the formation of which is, however, limited sterically. The trans-configurations of the trans-form (V), on the other hand, enter into the Diels-Alder synthesis at temperature rise. They proceed thereby into the trans-

B

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configuration of the flat cis-form (VI) which favors the said reaction. The authors presume 2 flat forms for chloroprene and isoprene: a trans-form (VII) and a cis-form (VIII) (X = Cl, CH₃) exactly as with 2,3-dimethyl-butadiene (IX) and (X). Of these forms, (VII) and (IX) are prevalent at room temperature. The authors discuss the correlations of these forms with the Raman- and IR-spectra (Table 2) which were recorded on the Soviet spectrograph of type MCTT (ISP-51)² and Hilger spectrograph of type E-612 (Ye-612)². The physical properties of the substances investigated are mentioned finally. There are 1 table and 8 references, 4 of which are Soviet. ✓ B

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk (Institute of Combustible Minerals, AS USSR). Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N.D. Zelinskiy, AS USSR)

PRESENTED: December 2, 1959, by B. A. Arbuzov, Academician

SUBMITTED: December 7, 1959

Card 3/3

BATUYEV, M.I.; AKHREM, A.A.; KAMERNITSKIY, A.V.; MATVEYEVA, A.D.

Optical study of the conformations of cyclohexanone and some of its derivatives. Dokl.AN SSSR 133 no.5:1077-1080 Ag '60.

(MIRA 13:8)

1. Institut goryuchikh iskopayemykh Akademii nauk SSSR i Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.
(Cyclohexanone)

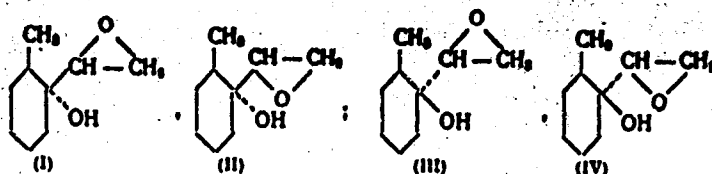
S/020/61/137/005/017/026
B103/B208

AUTHORS: Batuyev, M.I., Akhrem, A.A., and Matveyeva, A.D.

TITLE: Optical study of the conformations of 2-methyl-1-hydroxy-
-cyclohexyl-ethylene oxides

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 5, 1961, 1113 - 1116

TEXT: It is the purpose of the present study to define the structure of
the following glycidic alcohols:



which had been obtained by oxidation by peracetic acid in chloroform from

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S/020/61/137/005/017/026
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cis-2-methyl-1-vinyl cyclohexanol: (I) and (II); trans-2-methyl-1-vinyl-cyclohexanol: (III) and (IV); and which were found to have the above structural formulas. All four alcohols have different melting points. Their structures were studied by their Raman spectra measured on the USSR spectrograph of the type WCN-51 (ISP-51), and on an 8612 Hilger spectrograph. It is concluded from the data (Table 1) that a hydrogen bond exists between the hydroxyl group of these alcohols in liquid state and the oxygen atom of the oxide ring. This is confirmed by the fact that the O - H frequency is a blurred narrow band which is quite different in the two trans-isomers. It is narrow ($\sim 45 \text{ cm}^{-1}$) in the low-melting isomer (IV) ($40.5 - 41^\circ\text{C}$), and broader ($\sim 200 \text{ cm}^{-1}$) in the high-melting isomer (III) ($75 - 75.5^\circ\text{C}$). This is assumed to indicate a predominance of the intramolecular H-bond in (IV), whereas in (III) the intermolecular bond prevails. This difference seems to exert a considerable effect on the melting points. This fact was used for the identification of (III) and (IV). If the different melting-points of (I) and (II) have the same reason, the higher-melting alcohol (I) ($43 - 43.5^\circ\text{C}$) is that with intermolecular H-bond,

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while the liquid (II) has the intramolecular bond. This assumption was confirmed optically. In a considerable part of the molecules of (II) in the liquid phase the O-H group is released from the intramolecular H-bond and enters the intermolecular H-bond. The threo-isomer is thus partly converted to the erythro-isomer, or to an isomer having a similar position of the oxide ring as the erythro-isomer. The conversion of the erythro-isomer to the threo-isomer can hardly be confirmed optically in the case of (I). The authors conclude from these facts that the two types of H-bond represent the most important stabilizing factors in the case of erythro-threo-isomerism. The energy of the H-bond is not high (~ 3 kcal/mole). These bonds therefore cause a considerable difference of the mentioned isomerism in crystalline state, but not in liquid or super-cooled-liquid state. The intramolecular bonds are, as a rule, not destroyed in 20% solutions of these alcohols in CCl_4 , which was also optically confirmed. The complexes of (I) and (III) with several members, which are associated by the intramolecular H-bond, are destroyed, while dimeric complexes are preserved, and monomers are formed. The authors conclude from the optical data that under their experimental con-

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ditions each of the four alcohols mentioned exist: in two conformations. The prevalent conformation are: in (I) - cis-ea (Fig. 1), in (III) and (IV) - trans-ee; in (II) both conformations appear to about the same extent. There are 1 figure and 6 Soviet-bloc references.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR
Institute of Mineral Fuels of the Academy of Sciences
USSR)
Institut organicheskoy khimii im. N. D. Zelinskogo
Akademii nauk SSSR (Institute of Organic Chemistry imeni
N. D. Zelinskiy of the Academy of Sciences USSR)

PRESENTED: November 28, 1960, by B. A. Arbuzov, Academician

SUBMITTED: December 29, 1960

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Optical study of the ...

S/020/61/137/005/017/026
B103/B208

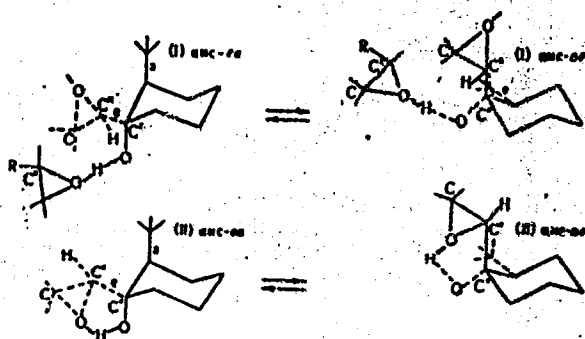


Fig. 1

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Optical study of the

S/020/61/137/005/017/026
B103/B208

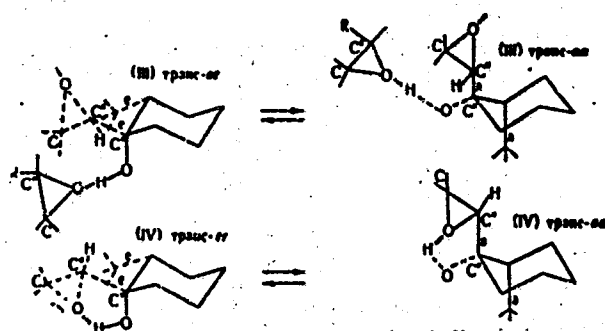


Fig. 1 cont'd.

Fig. 1. Legend: a) cis- b) trans-

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Таблица 1
Частоты колебаний гидроксильной, окисного цикла и циклогексанового кольца (в см⁻¹)



Группы А	1. Жидкое состояние				3. 10% раствор в CCl ₄			
	(I)	(II)	(III)	(IV)	(I)	(II)	(III)	(IV)
O-H	3390-3570; д.полоса	3625-3665; полоски L	3390-3560; д.полоса	3520-3605; полоска C	3641 (1°) 3645 (2°) 3612 (3°) 3621 (1)	3625 (1°) 3652 (2°) 3612 (3°) 3623 (0)	3642 (1°) 3663 (2°) 3613 (3°) 3621 (0)	3627 (1°) 3650 (2°) 3618 (3°) 3626 (0)
	1250 (2°) 1257 (3°) 1268 (2° дб)	1252 (2° дб) 1265 (3° дб)	1252 (7 дб) 1268 (1 дб)	1252 (1 дб) 1269 (6 дб)	1249 (1°) 1255 (5°) 1269 (1 дб)	1252 (1° дб) 1261 (5° дб)	1252 (5 дб) 1268 (0 дб)	1253 (1 дб) 1269 (4 дб)
	703 (8 дб) 714 (2 дб)	702 (8 дб) 713 (3 дб)	700 (1 дб) 718 (7 дб)	703 (1 дб) 718 (8 дб)	700 (4 дб) 714 (1 дб)	701 (4 дб) 715 (2 дб)	701 (1 дб) 719 (4 дб)	699 (1 дб) 715 (4 дб)

Table 1. Vibrational frequencies of the hydroxyl, the oxide ring, and the cyclohexane ring (cm⁻¹). Legend: 1) group; 2) in liquid state; 3) 20% solution in CCl₄; a) band; b) narrow bands; c) narrow band; Ab = doublet.

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BATUYEV, M.I.; AKHREM, A.A.; KAMERNITSKIY, A.V.; MATVEYEVA, A.D.

Optical study of conformations of cyclopentanone and α -chloro-
cyclopentanone. Izv.AN SSSR.Otd.khim.nauk no.6:1138-1141 Je '61.
(MIRA 14:6)

1. Institut goryuchikh iskopayemykh AN SSSR i Institut organicheskoy
khimii im. N.D.Zelinskogo AN SSSR.
(Cyclopentanone) (Isomers)

BATUYEV, M.I.; AKHREM, A.A.; KAMERNITSKIY, A.V.; MATVEYEVA, A.D.

Optical investigation of conformations of cyanohydrins of
some derivatives of cyclohexanone. Izv.AN SSSR.Otd.khim.nauk
no.10:1813-1816 0 '61. (MIRA 14:10)

1. Institut goryuchikh iskopayemykh AN SSSR i Institut organicheskoy
khimii im. N.D.Zelinskogo AN SSSR.
(Cyanohydrins) (Cyclohexanone)

BATUYEV, M.I.

One of the proofs of the hypothesis on the static effect
of the ~~π-π~~-conjugation, based on a mechanistic under-
standing of the characteristic frequency. Reply to E.N.
Prilezhaeva by M.I. Batuev. Zhur.ob.khir. 32 no.2:665-669
F '62. (MIRA 15:2)

(Spectrum analysis)

BATUYEV, M.I.

Cyclohexatriene structure of benzene (reply to F. Cheshko).

Zhur.ob.khim. 32 no.10:3457-3461 0 '62. (MIRA 15:11)

(Benzol.)

(Chemical structure)

BASIN, Ya.B. REEL #39
to

END